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# FINAL REPORT FOR AFOSR AASERT GRANT No. F49620-95-1-0369

### Prepared for

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September 1998

#### I. INTRODUCTION

Funds provided by DOD under this AASERT grant provided support for graduate students to be involved in a research program at the University of Illinois that is focused on fabricating microdischarge devices and arrays on silicon. Our goal is to combine two disparate and seemingly incompatible technologies — discharge physics and engineering with silicon planar processing technology — to produce a new generation of on-chip devices and systems. This work has proven to be tremendously successful which is partially attributable to AASERT funding.

#### II. RESULTS AND DISCUSSION

The primary result of this research effort is the demonstration and development of small discharge devices integrated into silicon using techniques that are well known in the semiconductor industry. Specifically, we have fabricated cylindrical discharges having diameters ranging from 20  $\mu$ m to 400  $\mu$ m on silicon and arrays of up to 5 elements on a single chip.

Both hollow cathode and planar cathode devices have been fabricated thus far. The hollow cathode discharges have cylindrical channels micromachined into a layered structure consisting of a metal anode, glass dielectric and silicon substrate. Typically, the channel extends 2-4 mm into the silicon. Devices having diameters as small as 20  $\mu$ m have been made to date and their properties are extraordinary. The reprints in the Appendix describe these in more detail but a few should be mentioned:

- 1.  $400 \, \mu m$  diameter devices operate as hollow cathodes for pressures above 50 Torr.
- 2. The specific power loadings are unprecedented, ranging from 1-4 kW-cm⁻³ for a 400  $\mu$ m diameter device to approximately 1 MW-cm⁻³ for a discharge ~20  $\mu$ m in diameter.
- 3. Because of the small diameters of these devices, they will operate continuously in air, and at N₂ gas pressures above one atmosphere and Ne pressures above 600 Torr. This feature alone makes these of interest for atmospheric sensors.

In more recent work, we have demonstrated that planar Si cathodes also work well. This configuration is well-suited for mass production because it is necessary for one to pattern on an Si substrate only the dielectric and anode films. With this approach, arrays having up to five elements have been produced by ultrasonic micromachining. These arrays are bright (easily seen

in ambient lighting) and because they exhibit a VI characteristic having a positive differential resistivity, the individual elements need not be ballasted individually.

Another mode of operation that we envision for these devices but have not yet tested, is a "flow through" geometry in which the discharge occurs primarily in a channel extending completely through the substrate. In this manner, gas can be flowed through the microdischarge and there decomposed by electron-molecule collisions and other reactions. We anticipate that this arrangement will be ideal for remediating environmentally hazardous gases and producing gas phase species such as ozone.

We believe the commercial potential of this technology is great and, accordingly, a patent application was submitted to the Patent and Trademark Office in May of 1977. A new disclosure was submitted to the University of Illinois in early summer this year and will likely be appended to the original patent application.

I want to express my thanks to Professor Thomas DeTemple for his collaboration on several phases of this work and am grateful to DOD and AFOSR, in particular, for their support of this work.

#### **APPENDIX:**

RECENT REPRINTS

#### Planar microdischarge arrays

#### J.W. Frame and J.G. Eden

Planar arrays of 400 µm diameter discharge devices fabricated on silicon with an anode-cathode spacing of 1mm and device separations as small as 0.8mm are reported. Operated in parallel with a single ballast and specific power loadings in the discharge up to ~40kW-cm⁻³, these arrays produce continuous emission from the atomic rare gases and transient molecules such as the rare gas-halide excimer, xenon-monoiodide (XeI).

Displays require arrays of high brightness pixels such as those offered by plasma display panels (PDPs). Pixel resolution < ~1 mm and array luminance > 250cd-m⁻² are now available with PDPs [1, 2] but the projected market and specifications for displays as well as manufacturing considerations have spurred research into competing technologies such as field emission devices. [3]

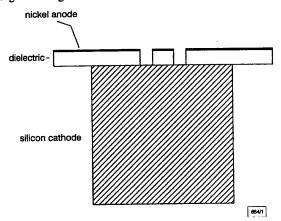


Fig. 1 Diagram of two microdischarge devices

Metal electrode is 0.4 µm thick evaporated film of Ni or 12 µm thick electrodeposited layer and is generally operated as anode

Recently, we reported [4-6] the operation of cylindrical microdischarge devices fabricated in Si and having diameters of 200-400um. Characterised by specific power loadings beyond 10kW cm⁻³, these devices produce continuous, intense visible and ultraviolet emission from atomic and molecular species in discharges in the rare gases, N2, and rare gas/I2 or O2 mixtures. Of particular interest is the fluorescence from transient diatomic molecules, such as the rare gas-halides [6] and -oxides and the rare gas dimers, [7] reported recently. One motivation for developing microdischarge devices in Si is the potential for integrating these sources of radiation (as well as electrons and ions) with electronic devices. However, a potential drawback of the design of [5, 6] for volume production is the hollow cathode, 0.5-4mm in depth, micromachined into the Si substrate. A simple yet remarkably effective device structure, amenable to fabrication by standard VLSI techniques, is described here. Planar arrays of these microdischarge devices have been operated by driving the individual elements in parallel with a single ballast.

A schematic diagram of two microdischarge devices is shown in Fig. 1. The silicon substrate serves as a planar electrode and the anode and cathode are separated by a dielectric (typically, glass or SiO₂). For the experiments reported here, the dielectric was glass ~1 mm in thickness. The second electrode is nickel (either a 4000 Å thick evaporated film or a 12 µm electroplated layer) and the effect of anode thickness on device performance will be described elsewhere. Cylindrical channels, ~400 µm in diameter, are produced in the metal film and dielectric by ultrasonic milling. Subsequently, an anodic bond is formed between the dielectric and an Si substrate. Discharges are produced in these structures with either polarity but operation of the arrays is most stable when the Ni electrode acts as the anode. All experiments were conducted at room temperature with a static gas fill, and the discharge elements were driven in parallel with a single ballast.

The IV characteristics for a single discharge element are presented in Fig. 2 for several Ne pressures between 20 and 600Torr. Two distinct regimes of operation are apparent, both of which are characterised by positive differential resistivities. For gas pressures and currents below 100Torr and 2mk, respectively, the device voltage is typically > 400V and the discharge resistivity is large

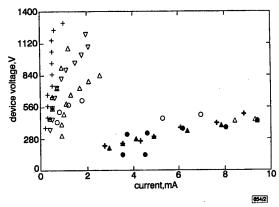


Fig. 2 IV characteristics for single 400 µm diameter microdischarge operating in Ne



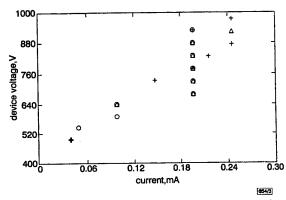
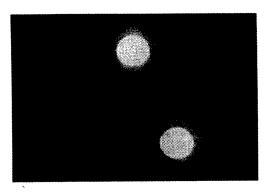


Fig. 3 Data similar to Fig. 2 for two 400 µm discharge elements separated by ~1.2mm and operated in parallel at low Ne pressure (20 -50 Torr) and current (<  $250\mu A$ )

- + 20Torr
- △ 30Torr O 40Torr + 50Torr

(~1 M $\Omega$  for  $P_{Ne} = 50$ Torr). Operation at higher pressures (100– 600Torr) is characterised by a factor of ~20 decline in the differential resistivity. In the 2 - 4 mA interval, the discharge voltage is ~180 - 270 V (for Ne pressure of 200 - 600Torr) which is comparable to the scanning and sustaining voltages typical of pixels in PDPs [1, 2]. Note that for currents > 9mA, the specific power loading of the discharge is ~40kW cm⁻³. Similar data for two  $400\mu m$  diameter discharges spaced by 1.2 mm and operating at low pressure (20-50Torr Ne) are given in Fig. 3 for currents up to 0.25mA, and Fig. 4 shows CCD images of two microdischarge arrays. The top portion of Fig. 4 is an image of a two element device operating with a discharge current of 0.15mA and a Ne pressure of 20Torr. A five element array in which the element spacing (~1-1.5mm) was varied is pictured in the lower half of Fig. 4. The gas pressure and discharge current for the five element array are 17Torr of Ne and 0.11mA, respectively, and coupling of the discharges of adjacent devices, presumably due to stray capacitance, is noticeable. Both of the devices in Fig. 4 were fabricated with a 0.4 µm thick Ni anode, and stable operation of the arrays was readily obtained over the full range of pressures and currents of Fig. 3. At higher pressures and currents (> 0.3mA), differences in intensity among the array elements were evident. Arrays consisting of discharge devices with the thick (12 µm) electroplated Ni anode layer were operated at an element spacing of 0.8mm, and no coupling between adjacent discharges was observed.

Not only have microdischarge arrays been operated on the rare gases, but also with Xe/I2 gas mixtures. CW emission from the XeI



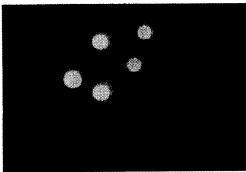


Fig. 4 CCD images of two and five element microdischarge arrays operating with 17 Torr of Ne

Magnification is ~40 and 20 for top and bottom parts, respectively; discharge spacing for five element array was varied intentionally

excimer species has been generated and, as first reported in [6], virtually all of the fluorescence from the discharge in the 200–800 nm region is produced by the  $B \to X$  transition of the molecule ( $\lambda_{max} = 254$ nm).

In summary, arrays of microdischarge devices consisting of as many as five elements have been operated continuously on the rare gases and the transient (excimer) molecule XeI (254nm). Extending these results to considerably larger arrays appears to be quite feasible. Fabricated by techniques suitable for mass production, the arrays are attractive for lighting and display applications but, because of the large specific power loadings available, will undoubtedly also be useful for the decomposition of environmentally hazardous gases and vapours such as volatile organic compounds.

Acknowledgments: The expert technical assistance of K. Voyles, B. Bozeman, and K. Kuehl and discussions with M.J. Kushner and J.T. Verdeyen are gratefully acknowledged. This work was supported by the U.S. Air Force Office of Scientific Research under grants F49620-97-1-0261 and F49620-98-1-0030.

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7 EL-HABACHI, A., and SCHOENBACH, K.H.: 'Emission of excimer radiation from direct current, high pressure hollow cathode discharges', Appl. Phys. Lett., 1998, 72, pp. 22-24 (the discharge devices in this work consisted of molybdenum electrodes and mica as the dielectric)

## Microdischarge devices fabricated in silicon

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Cylindrical microdischarge cavities 200–400  $\mu$ m in diameter and 0.5–5 mm in depth have been fabricated in silicon and operated at room temperature with neon or nitrogen at specific power loadings beyond 10 kW/cm³. The discharges are azimuthally uniform and stable operation at N₂ and Ne pressures exceeding 1 atm and ~600 Torr, respectively, has been realized for 400  $\mu$ m diameter devices. Spectroscopic measurements on neon discharges demonstrate that the device behaves as a hollow cathode discharge for pressures >50 Torr. As evidenced by emission from Ne and Ne⁺ ( 2P , 2F ) states as well as N₂ ( $C \rightarrow B$ ) fluorescence (316–492 nm), these discharge devices are intense sources of ultraviolet and visible radiation and are suitable for fabrication as arrays. © 1997 American Institute of Physics. [S0003-6951(97)02435-2]

Because of their non-Maxwellian electron energy distribution functions and high current densities, hollow cathode discharges have, for decades, been of interest as lamps and for the excitation of lasers. 1 Capable of generating beams of electrons having energies comparable to the cathode fall potential, these discharges have proven to be efficient sources for driving rare gas and metal ion laser transitions.^{2,3} However, since the maintenance of a hollow cathode discharge requires that the product of the gas pressure p and cathode diameter d be within a specified range, operation has generally been limited to pressures of no more than several tens of Torr. In 1959, White⁴ examined hollow cathodes having diameters of 750 µm and, recently, Schoenbach et al.5 reported the characteristics of hollow cathode devices machined in molybdenum and having cathodes typically 700 μm in diameter. In Ref. 5, reducing the cathode aperture to 75 µm permitted operation at air pressures as high as 350 Torr.

This letter reports the fabrication of microdischarge devices in silicon and their operation in Ne and N2. Silicon was chosen because of its thermal conductivity and resistance to ion sputtering,6 the potential for integrating microdischarges with external electronics, and the ability to fabricate devices with small cathode diameters by a variety of well-established processing techniques such as ultrasonic milling, ultraviolet (UV) laser ablation, and plasma etching. In these experiments, cathode diameters ranging from 200 to 400 µm have been studied and operation of stable, azimuthally uniform discharges is obtained for Ne pressures up to 600 Torr, N₂ pressures >1 atm, and specific power loadings of ~10 kW/cm³. Emission spectroscopy and the observation of fluorescence from excited states of Ne+, in particular, demonstrate that 400 µm diameter devices behave as hollow cathode discharges for Ne pressures >50 Torr.

Figure 1 is a schematic diagram of a representative device. Cylindrical channels, 200 or 400  $\mu$ m in diameter (d) and 0.5-5.0 mm in depth (L), were milled ultrasonically in metallurgical grade polycrystalline silicon (>98% purity). For most of the devices fabricated to date, thin (~0.2  $\mu$ m)

Cr/Ni films evaporated onto glass served as the anode and electrical contact to the Si cathode was made with a copper block and conductive epoxy. When evacuated (base pressure  $\sim 10^{-6}$  Torr) and backfilled with the desired gas, these devices produce intense fluorescence, readily visible in ambient lighting. Emission spectra for devices operating under a range of conditions were recorded by imaging (with a 20 cm focal length lens) the discharge aperture onto the slits of a 0.25 m spectrograph coupled to a diode array detector. Spatially resolved profiles of the discharge fluorescence were obtained by viewing the discharge along its axis with a microscope objective and a CCD camera.

The I-V characteristics of a 400  $\mu$ m diameter device having a length of 1.75 mm are presented in Fig. 2 for Ne pressures ranging from 20 to 100 Torr. Similar data were obtained at higher pressures and currents up to 4 mA. Over the entire current and pressure  $(0.8 \le pd \le 4 \text{ Torr cm})$  range studied, the I-V characteristics exhibit a positive differential resistivity⁵ and, for the data of Fig. 2, the specific power loading of the discharge ranges from ~1 to 4 kW/cm³ on a cw basis. At higher pressures (>200 Torr) and currents (4 mA), the power loading exceeded 10 kW/cm³ for a 200  $\mu$ m diameter device. As a check for power loss through the bulk of the device, an electrical probe was inserted into the cylindrical cavity and the resistance between the probe and rear contact was measured to be 150  $\Omega$ . Consequently, for the currents typical of discharge operation, the power dissipation in the Si base of the device is negligible. Stable glow discharges in Ne are reliably generated in 400  $\mu$ m diameter

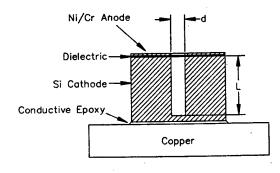


FIG. 1. Diagram of a single microdischarge device in silicon.

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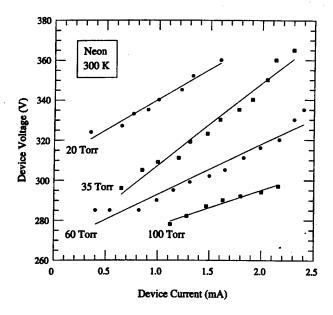


FIG. 2. I-V characteristics for a 400  $\mu m$  diameter discharge (1.75 mm in length) in Ne for pressures ranging from 20 to 100 Torr.

devices at pressures above 500 Torr. Also, the discharges are azimuthally uniform with peak intensity produced on axis.

Emission spectra serve as a convenient monitor of the behavior of the discharge and, in particular, are a sensitive diagnostic of the transition from hollow cathode operation to a normal glow. Although >90% of the total emission produced by a Ne discharge lies in the red, it is in the ultraviolet (UV) that one finds transitions that are most sensitive to the electron energy distribution function and, hence, to hollow cathode operation. Consider, for example, Fig. 3 which presents a comparison of the UV spectra in the 320-380 nm region generated by a Ne hollow cathode discharge (spectrophotometer lamp), a commercial positive column ("pen light") discharge, and a cw microdischarge device (d

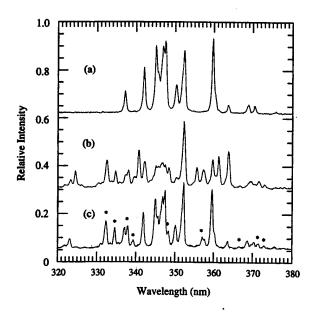


FIG. 3. Comparison of the Ne emission spectra in the near-UV (320–380 nm) produced by: (a) a positive column (pen lamp) discharge, (b) a hollow cathode (spectrophotometer lamp) discharge, and (c) a microdischarge device ( $d=400~\mu\text{m},~L=3.5~\text{mm}$ ) operating at 50 Torr, 235 V, and 3.0 mA. The strongest Ne⁺ lines are indicated by an asterisk in spectrum (c).

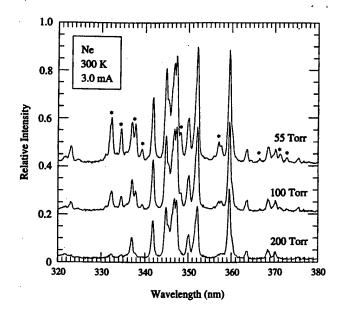


FIG. 4. Variation of the microdischarge emission spectrum in the 320–380 nm region with increasing Ne pressure. The device parameters and operating conditions are the same as those for Fig. 3. Neon ion transitions are indicated in the 55 Torr spectrum by an asterisk.

=400  $\mu$ m, L=3.5 mm, 235 V, 3 mA) operating at 55 Torr (pd=2.2 Torr cm). These spectra indicate that the microdischarge behaves as a hollow cathode at pressures beyond 50 Torr, or roughly an order of magnitude larger than those accessible with conventional discharge devices. Specifically, all of the lines present in the microdischarge spectrum arise from Ne and Ne+ but the latter are present only in the hollow cathode [Fig. 3(b)] and microdischarge spectra. The strongest Ne⁺ features (at 334.55 and 332.38 nm) are the result of transitions originating from  ${}^{2}P^{0}$  and  ${}^{2}F^{0}$  states of the ion which lie > 30 eV above the Ne  $(2p^6)$  ground state. As illustrated in Fig. 4, these and other ion lines in the 322-357 nm wavelength interval (indicated by an asterisk in the 55 Torr spectrum) gradually weaken with increasing gas pressure until, at 200 Torr (pd=8 Torr cm), the microdischarge spectrum is virtually indistinguishable from that produced by a positive column discharge [Fig. 3(a)]. One concludes, therefore, that the electron temperature in the 55 Torr microdischarge is substantially higher than that characteristic of a positive column.

Discharges in  $N_2$  and air produce strong  $N_2$  ( $C \rightarrow B$ ) emission in the UV and visible (316–492 nm;  $-6 \le v' - v'' \le 1$ ) and stable microdischarge operation in pure  $N_2$  has been obtained at pressures > 1 atm. Atomic Si emission lines in the 240–300 nm region are extremely weak or not detectable which is consistent with the low sputtering rate for Si by rare gas ions. However, several strong Cr and Ni transitions between 280 and 311 nm are observed, the most intense of which lie in the 308–311 nm spectral interval and are attributed to Ni. Erosion of the metal anode limits the lifetime of the device which can be ameliorated by resorting to poly-Si electrical contacts.

In separate tests, a  $\sim 1.1~\mu m$  thick SiO₂ film grown on standard 10 cm diameter, integrated circuit grade silicon wafers (n type,  $\rho \sim 5\Omega$  cm) served as the dielectric. For this oxide thickness, the dielectric breakdown voltage exceeds 1

kV [breakdown voltage≈1.5 thickness of oxide, expressed in nm (Ref. 8)]. Stable discharges, limited in length by the wafer thickness (0.5 mm), were again generated. These results and the variety of techniques available for producing high quality oxide films on silicon suggest that the realization of a family of devices in which optical sources, detectors, and electronic devices are incorporated onto a single chip by batch processing, is now feasible. Finally, the ability of microdischarges to operate as a hollow cathode or normal glow discharge at high pressures and power loading (>10 kW/cm³) suggests that the production of transient molecular species is now practical on a cw basis in a lamp. A key issue yet to be pursued is the limit on gas pressure and discharge dimensions. The latter is of particular interest since, for small discharge diameters, the cavity will modify the atomic or molecular spontaneous emission rates (by cavity quantum electrodynamics). Consequently, as d approaches the wavelength of the prominent atomic transitions (≤1  $\mu$ m for Ne), perturbations of the discharge emission spectrum can be expected to occur.

Several valuable discussions with J. T. Verdeyen and M. J. Kushner and the technical assistance of K. Voyles and K. Kuehl are gratefully acknowledged. This work was supported by the U.S. Air Force Office of Scientific Research under Grant No. F49620-95-1-0238, the National Science Foundation under Grant No. ECD 89-43166, and the University of Illinois Industrial Affiliates Program.

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# Continuous-wave emission in the ultraviolet from diatomic excimers in a microdischarge

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Emission on the  $I_2$  ( $D' \rightarrow A'$ ), XeI ( $B^2 \Sigma_{1/2}^+ \rightarrow X^2 \Sigma_{1/2}^+$ ) and XeO ( $2^3 \Pi \rightarrow 1^3 \Pi$ ) bands, peaking in the ultraviolet at 342, 253 and 238 nm, respectively, has been generated on a continuous basis in a microdischarge with a static gas fill. Discharges are produced in Kr/I₂, Xe/I₂, or Xe/O₂ gas mixtures by cylindrical devices 400  $\mu$ m in diameter and fabricated in silicon. Rare-gas-halide and -oxide microdischarge lamps are attractive ultraviolet or vacuum ultraviolet sources and XeI, in particular, appears to be a potential replacement for Hg resonance line radiation (253.7 nm). © 1998 American Institute of Physics. [S0003-6951(98)02021-X]

For more than two decades, the rare-gas-halide molecules have been known to be efficient sources of ultraviolet (UV) and vacuum ultraviolet (VUV) radiation. Although the development of laser systems has been the focus of efforts to date, the potential of these species as the basis for lamps has also been recognized. Since the demonstration in 1980 of a KrF lamp excited by a pulsed (100-200 ns) longitudinal discharge in a quartz capillary by Gerber et al., 1 rare-gashalide lamps emitting at 193 nm (ArF), 222 nm (KrCl), and 248 nm (KrF), and driven by dielectric barrier² or microwave^{3,4} discharges have been developed. With regard to the latter, Kumagai and Obara³ reported microwaveexcited KrF and ArF lamps that produce tens of watts of average power in pulses of ~6 ms duration (full width at half maximum) at a repetition frequency of 100 Hz. Recently, glow discharge and electron-beam-pumped lamps,⁵ as well as pulsed discharges in supersonic expansions,6 were also demonstrated. For a variety of commercial and medical processes (such as polymer curing, germicidal applications, and semiconductor processing) requiring incoherent radiation in the spectral region below 350 nm, compact and efficient sources having a high duty cycle are desirable.⁷

In this letter, the generation of cw emission in the midto-deep UV from rare-gas-halide, halogen dimer, and raregas-oxide molecules produced in a microdischarge is described. Specifically, emission on the  $D' \rightarrow A'$  transition of  $I_2$ (342 nm), the  $B \rightarrow X$  transition of xenon monoiodide (XeI, 253 nm), and the  $2^{3}\Pi \rightarrow 1^{3}\Pi$  band of xenon oxide (XeO, 238 nm) is produced in Kr/I₂, Xe/I₂, or Xe/O₂ gas mixtures (respectively) in microdischarge devices fabricated in silicon. The XeI molecule is of particular interest because: (1) its peak emission wavelength is nearly coincident with that for the  $6p^{3}P_{1}\rightarrow 6s^{1}S_{0}$  resonance line of Hg; (2) the formation and fluorescence efficiencies for the molecule are among the highest for the rare-gas halides;8,9 and (3) the walls of the Si discharge are effectively passivated by SiI₄, a low volatility product of the reaction of iodine molecular precursors with silicon.

Recently, the characteristics of Ne and N₂ discharges in

cylindrical devices micromachined in Si were reported ¹⁰ and the microdischarge devices for these experiments were fabricated in 99.999% Si by similar processes. Briefly, cylindrical channels 400  $\mu$ m in diameter are machined ultrasonically to form the discharge cathode and a Cr/Ni film serves as the anode. The purity of the rare gases and  $I_2$  was research grade and 99.99%, respectively. Each device was mounted in a Pyrex glass envelope having a Suprasil grade quartz window. The tube was then evacuated to  $\sim 10^{-6}$  Torr prior to backfilling with the gas mixture of interest. Spectra were acquired with a 0.25 m spectrometer and a multichannel diode array. When the spectrograph is operated in first order, the overall resolution of the detection system is  $\sim 0.4$  nm.

Stable, dc discharges are readily obtained in mixtures of one or more rare gases and  $I_2$  or  $O_2$ . Figure 1 shows the visible and UV emission spectrum  $(200 \le \lambda \le 850 \text{ nm})$  recorded for a 50 Torr Xe,  $\sim 1$  Torr  $I_2$  gas mixture and a discharge current of 3.8 mA. The power dissipated in this 400  $\mu$ m diam plasma was 2.6 W and the specific power loading

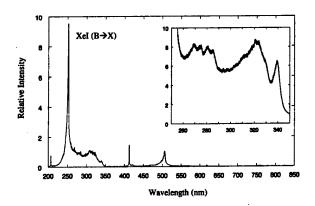


FIG. 1. Emission spectrum in the  $\sim 200-850$  nm wavelength interval for a microdischarge in a 50 Torr Xe/ $\sim 1$  Torr I₂ gas mixture. The discharge voltage and current are 700 V and 3.8 mA, respectively. The spectrum is dominated by the  $B \rightarrow X$  transition of Xel but emission from atomic iodine is also noticeable. This spectrum has not been corrected for the response of the detection system, which falls rapidly for  $\lambda < 300$  nm. The features peaking at  $\sim 412$  and  $\sim 506$  nm are the iodine resonance line and XeI( $B \rightarrow X$ ) emission, respectively, appearing in second order and the inset is a magnified portion (250–350 nm) of the spectrum.

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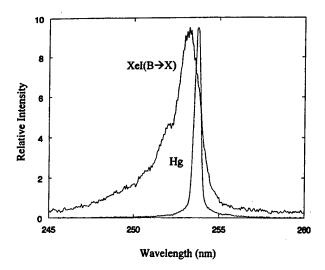


FIG. 2. Expanded view of the  $Xel(B \rightarrow X)$  fluorescence spectrum. The Hg resonance line at 253.7 nm, produced by a low-pressure capillary discharge, is included for comparison. Both the XeI and Hg spectra have been arbitrarily normalized to the same relative intensity.

of the discharge was  $\sim 1.7 \text{ kW cm}^{-3}$ . Because this spectrum was obtained with a diffraction grating having a blaze wavelength of 400 nm, the trace understates the relative strength of the deep UV emission. Nevertheless, >90% of the discharge fluorescence lies between 250 and 350 nm and the dominant feature is the  $B^2\Sigma_{1/2}^+ \rightarrow X^2\Sigma_{1/2}^+$  emission band of XeI, which peaks at ~253.2 nm. Weaker features to the red of the XeI  $(B \rightarrow X)$  transition arise from XeI and I₂. Between ~265 and 280 nm (cf. inset to Fig. 1) lies structure due to the  $C \rightarrow A$  band of XeI (whose origin is  $263 \pm 3$  nm)⁸ and the  $F \rightarrow B$  transition of I₂. At lower overall pressures (several Torr), it has been observed^{9,11} that peak XeI  $(B \rightarrow X)$  emission is blueshifted ( $\lambda_{max} \sim 251.8 \text{ nm}$ ),  $C \rightarrow A$  fluorescence extends further to the red, and spectral undulations in the intensity are more pronounced. The continuum peaking between 320 and 325 nm is produced by the XeI  $(B \rightarrow A)$  emission; the origin of this band has been reported by Tamagake et al.8 to be 320±5 nm. Note also in Fig. 1 the absence of  $Xe(6p\rightarrow 6s)$  emission in the near infrared.

A higher resolution (and expanded) view of the XeI (B)  $\rightarrow X$ ) fluorescence spectrum is illustrated in Fig. 2. The  $6p^{3}P_{1} \rightarrow 6s^{1}S_{0}$  resonance line of Hg (253.7 nm), produced by a low-pressure lamp, is included for the sake of comparison. The XeI profile is consistent with chemiluminescence spectra obtained at pressures above 20 Torr by Setser and co-workers^{8,11} who note that¹¹ "...vibrational relaxation of XeI(B) is nearly complete at ~100 Torr of Ar...' Undulations visible on the short-wavelength side of the XeI 253 nm band arise predominantly from  $B \rightarrow X$  transitions originating from low vibrational levels in the upper state ( $v' \leq 3$ ). Pholaser spectroscopy¹² toassociation and spontaneous emission^{8,13} studies of XeI have determined the vibrational frequency  $(\omega_e)$  and  $T_e$  for the B state to be  $112\pm10$  cm⁻¹ and  $\sim 40 \ 200 \ \text{cm}^{-1}$ , respectively.

Of primary interest is the efficiency with which XeI(B) is produced and radiates. The flowing afterglow experiments of Ref. 8 found the branching ratio for the formation of XeI(B) from the "harpoon" reaction of  $Xe(6p^3P_2)$  with  $I_2$  to be 80%—among the highest in the rare-gas—halide family. It is also known that the excimer formation rate constant

exceeds 10⁻¹⁰ cm³ s⁻¹, which corresponds to an effectivecross section beyond 100 Å² (Ref. 9). These considerations, combined with the near coincidence of XeI  $(B \rightarrow X)$  peak fluorescence with the Hg resonance line at 253.7 nm, suggest that a XeI lamp is interchangeable with the low-pressure Hg UV source in those applications for which phosphors or sensitizers have been optimized for excitation at 254 nm. Preliminary absolute power measurements have been made with a calibrated detector (200-800 nm) on microdischarges operating with a 50 Torr Xe, ~3 Torr I₂ gas mixture. For  $\sim 500$  mW of input power to the device,  $\sim 270 \mu W$  of output power, virtually all of which is emitted in the vicinity of 253 nm, is recorded  $\sim 1.4$  cm from the device ( $\sim 4$  mm from the lamp window), which corresponds to an observation solid angle of ~0.6 sr. Comparison of this result with a Hg microdischarge is not presently possible because the construction of the device does not permit significant heating. However, a Ne microdischarge operating under the same conditions produces 28  $\mu$ W of power (primarily in the visible). Furthermore, similar measurements on commercial, positive column discharge lamps show that the luminous efficiencies (wavelength-integrated emission normalized to input power) for low-pressure Ne and Hg lamps are comparable ( $\sim 30\%$  greater for Hg than that for Ne). Although preliminary, these results suggest that a XeI microdischarge lamp will be competitive with sources based upon the Hg 254 nm line.

Another attractive feature of the XeI species insofar as lamp applications are concerned is the benign chemistry of iodine molecular precursors (such as I2 and HI) with Si. The reaction of HI with Si, for example, is known to produce SiI₄ which has a vapor pressure of  $\sim 1.4 \times 10^{-2}$  Torr at 300 K (Ref. 14). For this reason, HI plasmas have been proposed as damage etchant for Si and no etching (<10 nm/min) is observed¹⁴ for HI pressures above 12 Pa  $(9 \times 10^{-2} \text{ Torr})$ , which is roughly an order of magnitude lower than the partial pressures employed here for the molecular iodine precursors. Stated another way, HI and I₂ react with the walls of the discharge device to form a low volatility passivating layer which appears to minimize the loss of iodine precursor and Si erosion, thereby extending device lifetime and permitting static fill operation. Recent surface analytical studies of the interaction of I2 with Si by Chakarian et al. 15 and Rioux and co-workers 16 reveal the formation of SiI, SiI₂, and SiI₃ when I₂ adsorbs onto Si(111), whereas the only species formed in significant quantities when I2 reacts with Si(100) is SiI. In Ref. 16, etching was observed only at temperatures >700 K.

IV characteristics for the Xe/I₂ discharge are shown in Fig. 3 for several values of the Xe partial pressure and  $P_{\rm I_2}$  fixed at ~1 Torr. For discharge currents above ~5 mA, the characteristics are identical to within experimental uncertainty and exhibit a slight positive differential resistivity. At lower currents (~100  $\mu$ A-4 mA), the data for the various pressures diverge and the inset to Fig. 3 illustrates the considerably higher voltages that are required for operation at  $p_{\rm Xe}=1$  Torr.

In Kr/I₂ gas mixtures, strong emission on the  $D' \rightarrow A'$  transition of I₂ is observed. Although only the 280-360 nm spectral region is shown in Fig. 4, the I₂  $(D' \rightarrow A')$  band,

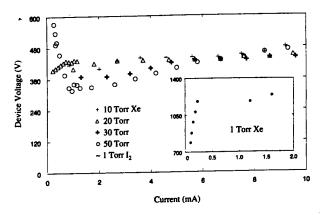


FIG. 3. VI characteristics for a discharge in  $XeI_2$  mixtures for Xe partial pressures ranging from 1 to 50 Torr. The  $I_2$  partial pressure is fixed at  $\sim 1$  Torr.

peaking at 342 nm, and the iodine resonance line at 206 nm are responsible for virtually all of the fluorescence detected from ~200 to 850 nm. Emission from KrI(B) is not observed because the  $B^2\Sigma^+$  state is predissociated. Fluorescence from the  $2^3\Pi$  ion pair state of XeO has also been produced in Xe/O₂ and Ne/Xe/O₂ gas mixtures. Maximum intensity on the  $2^3\Pi \rightarrow 1^3\Pi$  transition of the molecule was generated for 270 Torr Ne/22 Torr Xe/14 Torr O₂ gas mixtures and the spectral peak lies at ~238 nm. This transition was identified by Golde and Thrush, ¹⁷ analyzed by Xu et al. ¹⁸ in a flowing afterglow, and has been observed in the supersonic expansion experiments of Ref. 6.

Optimization of the gas mixture for maximum excimer emission and device lifetime have, in general, not yet been attempted. However, microscopic examination of several microdischarges indicates that the present lifetime of a few hours is limited by erosion of the metal film anode. The use of other anode materials, such as poly-Si, should ameliorate this problem. Also, it is expected that the lifetime of XeI  $(B \rightarrow X)$  lamps will be extended considerably with Xe/HI/H₂ gas mixtures in which H₂ plays the same role as it does in the XeCl discharge laser, which is noted for the longevity of a single gas fill  $(>10^8$  shots).

In summary, cw emission from XeI,  $I_2$ , and XeO in the mid-to-deep UV ( $\sim 230-345$  nm) has been generated in rare-gas/ $I_2$  or  $O_2$  gas mixtures in Si microdischarge devices at total gas pressures  $\lesssim 300$  Torr. The high-power loadings

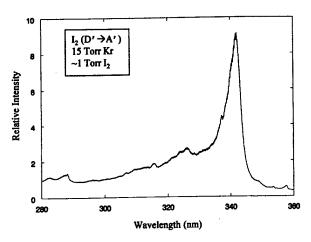


FIG. 4.  $I_2$  ( $D' \rightarrow A'$ ) fluorescence produced by a discharge in a 15 Torr Kr/ $\sim$ 1 Torr  $I_2$  gas mixture.

 $(1-10 \text{ kW cm}^{-3})$  available with 400  $\mu\text{m}$  diam discharges permit the continuous production of transient molecular species with modest power consumption. These results suggest that other excimer transitions, such as the KrO  $(2^3\Pi \rightarrow 1^3\Pi)$  band at  $\sim 180 \text{ nm}$  (Ref. 19) or the ArCl  $(B\rightarrow X)$  transition at 175 nm will be practical emitters in the VUV and offer a complement to the rare-gas dimers. The latter are formed by a three-body collision requiring high pressures (typically > 1 atm) for efficient excimer production.

In view of these results, XeI can be considered a candidate for replacing the Hg resonance lamp in several applications, whereas other heteronuclear excimers offer the potential for intense sources of incoherent radiation in the VUV. Neither HI nor I₂ are environmentally hazardous, which addresses an issue of increasing importance—the disposal of Hg-containing lamps. Furthermore, since Si is the host material for these devices, integrating rare-gas—halide microdischarges with other Si-based devices is an attractive option.

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